



Production of hydrogen-rich syngas using Zr modified Ca-Co bifunctional catalyst-sorbent in chemical looping steam methane reforming



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HIGHLIGHTS

- Promotion of Ca-Co with Zr represents high activity and significant stability in multiple cycles.
- The carbon deposition could be eliminated by direct reaction between CaO and methane.
- The influence of various process and synthesis variables on the catalytic activity is studied.
- High activity is obtained during 16 redox cycles for Ca-Co-Zr bifunctional catalyst-sorbent.

ARTICLE INFO

Keywords:

Bifunctional catalyst-sorbent
Hydrogen production
Calcium
Methane reforming
Chemical looping reforming
Zirconium promoter

ABSTRACT

High purity H₂ could be produced through modified chemical looping steam methane reforming (CL-SMR) process using calcium as an essential component in the structure of bifunctional catalyst-sorbents. Herein, we present an effective approach to the production of high purity hydrogen in chemical looping reforming of methane via modification of a bifunctional Ca-Co-Zr catalyst-sorbent. The synthesis of the samples including pure Ca, Ca-Co and zirconium modified Ca-Co with different molar ratios was performed using co-precipitation method. The influence of reaction variables such as steam to carbon molar ratio (S/C = 1–5), reaction temperature (500–750 °C) and lifetime of the samples are investigated on methane conversion and hydrogen yield. Moreover, Ca/Co mass ratio (0.11–9) is optimized and subsequently, different amounts of zirconium promoter (mass ratio = 2.25–18) are added to improve the bifunctional catalyst-sorbent structure. The characterization of samples was performed using XRD, FESEM, BET and EDX techniques. It is found that the addition of zirconium to the sample could improve the textural features and stability of bifunctional catalyst-sorbent. The results reveal that Ca-Co-Zr (via mass ratios of $\frac{Ca}{Co} = 9$ and $\frac{Ca}{Zr} = 4.5$) exhibits the highest catalytic activity among all tested samples and shows 98.3% methane conversion and 84.5% hydrogen yield at 700 °C. The cyclic life time results at 700 °C indicated that the Ca-Co-Zr (9,4.5) bifunctional catalyst-sorbent remained stable up to 16 cycles, while non-promoted samples showed fast deactivation after about 10 redox cycles. The coke formation is inhibited, while the reaction pathway changes to a combined reaction. In summary, the obtained results show the suitable efficiency of the synthesized catalyst in the modified CL-SMR process.

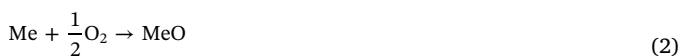
1. Introduction

Nowadays, fossil fuels are the most commonly used source of energy. The combustion of fossil fuels caused the increment in the concentration of CO₂ in the atmosphere, which has led to some global problems, such as climate change and global warming [1,2]. According to the importance of environment and the international warnings related to the global warming, the development of clean energies was considered recently. Hydrogen and renewable sources including bioenergy, solar, wind, geothermal, marine and hydropower energy are two

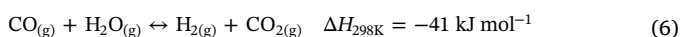
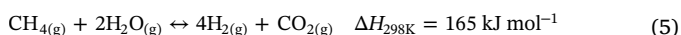
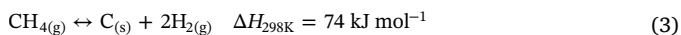
important categories of clean energy. Hydrogen is expected to have a key role in the world's future energy via replacing fossil fuels due to its easy conversion to heat and power [3–5]. It is also known as an environmental friendly fuel and high power density for transportation fuel and electricity generation. When hydrogen burns, its combustion by-product is water vapor, which is a non-toxic material. Hydrogen has a wide range of application in both petroleum refining and chemical industries such as alcohols, ammonia synthesis and many other important industrial productions. Hydrogen can be produced from several methods, such as reforming of hydrocarbon, gasification of biomass,

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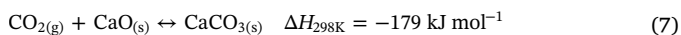
water electrolysis and thermochemical water splitting [6–11]. The production cost and the purity of hydrogen are important factors, which are highly regarded in various applications. Reforming of hydrocarbons such as CH₄ is known as one of the most economical methods for the producing of hydrogen. In this process, the purity of produced hydrogen in reformer could be approached to about 70% [12,13]. The post processing is needed for the enrichment of hydrogen concentration in the produced gas stream. The methane reforming process could be improved using chemical looping reforming (CLR) and sorption enhanced chemical looping reforming (SECLR) strategies. The CLR process is one of the most promising methods that can be applied to produce hydrogen with reducing the amount of released carbon. Chemical looping reforming of natural gas or light hydrocarbons such as methane is a new technology for partial oxidation of hydrocarbon fuels, which has been studied on the basis of chemical looping combustion [14,15]. Chemical looping steam reforming can be mentioned as a possible method for producing hydrogen from either conventional or renewable sources like biomass. Recently, CLR process has attracted considerable attention because of the significant reduction in separation costs by splitting the process into two consecutive oxidation and reduction steps [16,17]. In this process, a catalyst containing a solid metal oxide called oxygen carrier (OC) is applied as a source of undiluted oxygen to produce synthesis gas via alternative oxidation and reduction of oxygen carrier [18]. These two steps including partial oxidation of methane and re-oxidation of oxygen carrier are given by Eqs. (1) and (2), respectively.



In addition, other side reactions such as methane decomposition, steam methane reforming and water gas shift reaction would be participated in the reaction media [19].



A unique process is innovated when chemical looping reforming and in situ CO₂ sorption are combined, which is called sorption enhanced chemical looping reforming. The CO₂ sorption could be conducted through the direct reaction between an alkaline or alkaline earth metal and carbon dioxide at high reforming temperature. The sorbents of SECLR process require some specific properties such as: high capacity of CO₂ sorption, lower energy of regeneration, high thermal/mechanical stability, suitable CO₂ sorption kinetics and low production cost. According to this description, calcium oxide based sorbents are considered as the most promising high-temperature CO₂ sorbents [12,20]. The calcium oxide reacts with CO₂ in the following exothermic reaction:

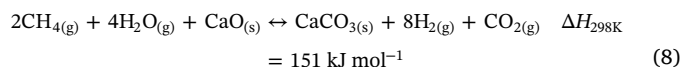


According to the upon reaction, the concentration of carbon dioxide could be reduced in the reaction media. The removal of produced CO₂ could proceed the water gas shift reaction towards producing more hydrogen according to Le Chatelier's principle [12,15].

In fact, the SECLR process is a novel method for producing hydrogen with high purity. This process includes three different steps: firstly, methane is partially oxidized by oxygen carrier and steam. At the same time, the produced CO₂ could be removed from reaction media using CO₂ sorbents. In the second step, the sorbents are transferred to the calcination reactor that is working at high temperature. The used sorbents are regenerated under endothermic reverse of reaction (7) and the calcium carbonate is decomposed to the CO₂ and CaO. Finally, the

oxygen carrier is reoxidized to its original state in the air reactor in accordance with reaction (2) before returning to carbonation reactor. In this regard, Dou et al. [21] reported that syngas with high purity of hydrogen (above 90%) was gained using NiO/NiAl₂O₄ as the oxygen carrier and CaO as sorbent at temperature of 500–600 °C. Antzara and his co-workers [22] synthesized NiO-based oxygen carrier supported on ZrO₂ and zirconium promoted CaO sorbent. Then they used the mixture of oxygen carrier and sorbent in the SECLR process. The process was performed over 20 consecutive reforming/regeneration cycles at 650 °C. The results showed the excellent stability of synthesized materials without deterioration during 20 cycles. They showed that hydrogen production through the combination of chemical looping reforming and CO₂ sorption could effectively reduce the production costs (about 55%) in comparison to conventional steam methane reforming.

Overall, the calcium oxide could be applied for producing hydrogen from methane according to the following reaction, which is the combination of the side reactions (Eqs. (4)–(7)) [23–25]:



Calcium oxide also has good characteristics such as ability to control the coke formation and low cost [26,27]. Thus, the calcium based bifunctional catalyst-sorbent has a high potential for producing hydrogen in chemical looping reforming process and operates through a mechanism similar to SECLR, as depicted in Fig. 1. Therefore, the reforming reactions, water gas shift reaction and CO₂ sorption could be performed simultaneously using the calcium based bifunctional catalyst-sorbent [23].

Some researchers studied the application of calcium as the promoter or sorbent in reforming process. Hafizi and his co-workers [28] investigated the influence of calcium position in the structure of Fe/Al₂O₃ oxygen carrier on its feasibility and activity in CL-SMR process. The results showed that the sample with 5 wt% Ca synthesized by co-impregnation method improved OC activity. In the study on the Ca-promoted Ni/α Al₂O₃ catalyst performed by Hou et al. [29] it was found that calcium can help to improve the nickel dispersion, avoid the fast sintering of it, and reinforce the interaction between Ni and Al₂O₃. Dang and the co-workers [30] studied a bifunctional catalyst (Co-CaO-Ca₁₂Al₁₄O₃₃) in sorption enhanced steam reforming of glycerol for producing hydrogen rich syngas. They found that at the Ca/Al ratio of 2.8, the sorption capacity and the catalytic activity are increased. Owing to the low tendency of calcium to participate in reforming reaction and the rapid decay of pure calcium oxide in CO₂ sorption [26], the addition of an active metal oxide as oxygen carrier is suggested. Selecting the appropriate oxygen carrier has a key role on the efficiency of CLR process. The proper oxygen carrier should have some characteristics including high methane conversion, adequate rate of oxidation and reduction, sufficient capacity for oxygen transportation, significant mechanical strength against the agglomeration and attrition and thermal/chemical stability. According to these properties some metal oxides such as Ni, Co, Mn, Fe and Cu can be used as feasible candidates [11,14,15,31]. Among these materials, Fe and Ni-based oxygen carriers are commonly investigated during the last years due to the high activity and resistance. The most important disadvantages of Ni-based oxygen carriers are coke formation and fast sintering at high reaction temperature. The Fe-based oxygen carriers are unsuitable for a long term cyclic operation due to their rapid reactivity degrade after a few redox cycles. Furthermore, Cu- and Mn-based oxygen carriers have relatively low melting point and thus have high tendency to sintering and agglomeration [17,32–34]. Some researchers are focused on the activity of Co-based oxygen carriers in the CL-SMR process. Also, catalysts containing cobalt possess remarkable advantages, such as high catalytic activity and low cost in addition to its high oxygen capacity [35–37]. Therefore, cobalt seems to be a suitable oxygen carrier for chemical looping process.

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